DESCRIPTION

CONTACT-CUMBUSTION TYPE GAS SENSOR AND MANUFACTURING METHOD OF SAME

TECHNICAL FIELD

5   The present invention relates to a contact combustion-type gas sensor installed

in an environment that is easily poisoned by a sensitivity degradation substance, and its

manufacturing method.

BACKGROUND ART

10   A solid polymer membrane-type fuel cell is, for example, provided with a stack

constituted by laminating a plurality of cells in which a solid polymer electrolyte

membrane is sandwiched between an anode and a cathode.   Hydrogen is supplied to the

anode as a fuel, and air is supplied to the cathode as an oxidizing agent, with hydrogen

15   ions generated by the catalytic reaction in the anode passing through the solid polymer

electrolyte membrane to the cathode, where an electrochemical reaction with oxygen

occurs, resulting in the generation of electricity.

Moreover, in fuel cells such as a solid polymer membrane type fuel cell,

although unreacted air, or off-gas, discharged from the cathode is generally exhausted to

20   outside the system, it is necessary when doing so to check that hydrogen gas is not

present in the off-gas.

As seen in Japanese Examined Patent Application Publication No. H06-52662

(hereinafter referred to as Patent Document 1) and Japanese Unexamined Patent

Application Publication No. H06-223850 (hereinafter referred to as Patent Document 2),

25   there has been developed a system in which a hydrogen detector is installed in the

exhaust system of the cathode side of a fuel cell to check that hydrogen gas does not exist in off-gas.

It is conceivable for such a hydrogen detector to employ a gas contact combustion-type gas sensor, which comprises a detecting element to which a catalyst is

5   bonded, and a temperature compensation element to which a catalyst is not bonded. Utilizing the heat of combustion when the gas to be detected (hydrogen in the case of a hydrogen detector) contacts the catalyst, the gas concentration of said gas to be detected is detected from the difference in the electrical resistance between the detecting element and the temperature compensation element.

10   Since organic silicon packing and hoses having heat resistance are used for the exhaust system of the cathode side, there exist in the measuring atmosphere of the contact combustion-type gas sensor small amounts of gaseous silicon compounds that precipitate and vaporize from the packing or hoses.   Such silicon compounds degrade the performance of the catalyst constituting the detecting element (so-called poisoning),

15   leading to a drop in detection sensitivity to flammable gas over time and a loss in measurement accuracy.

In order to cope with such problems, for a semiconductor sensor as seen in Japanese Unexamined Patent Application Publication No. S56-168542 (hereinafter referred to as Patent Document 3), that is, a sensor that detects changes in electrical

20   conductivity by adsorption of a gas to be detected, by housing the sensor in an environment containing dimethylsiloxane, which exerts a poisoning action on the sensor, to age the sensor, variations in characteristics such as sensitivity between sensors are lessened.

However, no such poisoning measures have been implemented for contact

25   combustion-type gas sensors that detect gas concentration from the difference in the

electrical resistance between the detecting element and the temperature compensation element utilizing the heat of combustion when the gas to be detected (hydrogen in the case of a hydrogen detector) contacts the catalyst.

In light of these circumstances, it is a first object of the present invention to

5   provide a contact combustion-type gas sensor that can maintain the initial sensitivity over a long period of time in the presence of silicon vapor.

It is a second object of the present invention to provide a contact combustion-type gas sensor that can minimize as much as possible the loss in sensitivity resulting from adhesion of silicon even when installed in an environment where organic

10   silicon compounds are present.

It is a third object of the present invention to provide a manufacturing method for the aforementioned contact combustion-type gas sensor.

DISCLOSURE OF THE INVENTION

15   The invention of claim 1 for solving these problems is a contact combustion-type gas sensor consisting of a gas detecting element that is housed in a case, said gas detecting element comprising an induction portion made of an oxidation catalyst powder and an insulating powder fixed to a heater that generates Joule heat, wherein said induction portion contains not less than 30 percent by weight of said oxidation catalyst.

20   In the invention of claim 2, said induction portion is formed by mixing said oxidation catalyst powder and said insulating powder with a solution and fixing the mixture onto the heater.

In the invention of claim 3, said induction portion is formed by fixing a slurry of said insulating powder to make a solidified body and then fixing a slurry of said

25   oxidation catalyst powder to the solidified body of said insulating powder, while in the

invention of claim 4, the outer surface of said induction portion is formed to have a high concentration of said oxidation catalyst.

In the invention of claim 6, an aging process is performed to converge the sensitivity loss due to silicon vapor.

In the invention of claim 7, said aging process is performed by energizing the heater in the gas detecting element to make it generate heat.

In the invention of claim 8, the concentration of said silicon vapor is set higher than the concentration of silicon in the environment used for measurement.

In the invention of claim 10, the contact combustion-type gas sensor is disposed in the gas outlet path on the cathode side of the polymer-type fuel cell to detect hydrogen in an environment that contains silicon vapor and hydrogen.

In the invention of claim 11, in a contact combustion-type gas sensor that carries a catalyst on a metal oxide sintered body carrier fixed to a resistance thermometer bulb, the contact combustion-type gas sensor is manufactured by being heated to 130°C to 500°C and then poisoned until fluctuations over time in the catalytic proficiency of said catalyst in an atmosphere that includes silicon compounds stabilizes to a prescribed value.

In the invention of claim 12, said atmosphere includes between 10 parts per million (ppm) and 30,000 ppm of at least one of hexamethyldisiloxane, hexamethyldisilazane, and hexamethyldisilane.

In the invention of claim 13, said atmosphere includes between 100 ppm and 20,000 ppm of at least one of hexamethyldisiloxane, hexamethyldisilazane, and hexamethyldisilane.

In the invention of claim 14, said atmosphere includes between 10 ppm and 30,000 ppm of at least one of hexamethyldisiloxane, hexamethyldisilazane, and

hexamethyldisilane, and between 100 ppm and 40,000 ppm of hydrogen.

In the invention of claim 15, the hydrogen concentration in said atmosphere is between 1,000 ppm and 20,000 ppm.

In the invention of claim 16, in a contact combustion-type gas sensor that carries a catalyst on a metal oxide sintered body carrier fixed to a resistance thermometer bulb, said metal oxide is at least one type chosen from alumina, silica, or zeolite, and poisoning is performed in advance until fluctuations over time in the catalytic proficiency of said catalyst in an atmosphere that includes silicon compounds stabilizes to a prescribed value.

In the invention of claim 23, the contact combustion-type gas sensor is disposed in the gas outlet path on the cathode side of the polymer-type fuel cell to detect hydrogen.

Effects of the Invention

The effects of the contact combustion-type gas sensor of the present invention will be specifically explained in the following.

The invention according to claim 1 prevents a loss in sensitivity by aging with a poisoning procedure and prevents fluctuations in the initial sensitivity during the measurement period and fluctuations in the sensitivity over time.

The invention according to claim 2 can fix an oxidation catalyst powder and an insulating powder to a heater simultaneously, and thereby simplify the manufacturing process.

The inventions according to claims 3 and 4 can attain a specified sensitivity while reducing the amount of costly oxidation catalyst that is used.

The invention according to claim 6 can prevent fluctuations in sensitivity due to silicon vapor in the use environment as much as possible.

The invention according to claim 7 can efficiently heat a gas detecting element to a prescribed temperature without requiring a heat source in the ageing device.

The invention according to claim 8 can more reliably prevent fluctuations in sensitivity over time.

The invention according to claim 10 can detect flammable gas, such as hydrogen, without incurring fluctuations in sensitivity over time even in the presence of silicon vapor emitted from packing or tubes in the gas outlet path on the cathode side of a polymer-type fuel cell.

The invention according to claim 11 can prevent fluctuations in the detection sensitivity for flammable gas over time even in an environment where silicon vapor is present.

The invention according to claim 12 can improve the processing yield and shorten the processing time.

The invention according to claim 13 can achieve more practical processing.

The invention according to claim 14 can substantially reduce processing time by promoting the formation of silicon oxide from combustion of hydrogen on the element surface.

The invention according to claim 15 can achieve a reduction in processing time while ensuring work safety.

The invention according to claim 16 can stably and accurately measure the concentration of flammable gas without causing fluctuations in sensitivity over time even in an environment where silicon vapor is present.

The invention according to claim 23 can detect flammable gas, such as hydrogen, without causing fluctuations in sensitivity over time even in the presence of silicon vapor emitted from packing or tubes in the gas outlet path on the cathode side of a

polymer-type fuel cell.

The preferred embodiments of the invention have been described and illustrated above, it should be understood that these are exemplary of the invention and are not to be considered as limiting. Additions, omissions, substitutions, and other modifications can

5 be made without departing from the spirit or scope of the present invention. Accordingly, the invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

10 FIG. 1 (A) and (B) are perspective and sectional views, respectively showing one embodiment of the gas detecting element constituting the contact combustion-type gas sensor of the present invention.

FIG. 2 is a graph showing changes in sensitivity over time in an environment including a poisoning substance after performing aging processing in an atmosphere

15 containing a high concentration of a poisoning substance on a gas detecting element manufactured by altering the concentration of oxidation catalyst powder contained in the induction portion.

FIG. 3 is graph showing changes in sensitivity over time in an environment including a poisoning substance for a gas detecting element manufactured by altering the

20 concentration of oxidation catalyst powder contained in the induction portion.

FIG. 4 is a sectional view showing another embodiment of the gas detecting element that constitutes the contact combustion-type gas sensor of the present invention.

FIG. 5 is a schematic drawing of the fuel cell system which is an example of applying the contact combustion-type gas sensor of the present invention.

25 FIG. 6 is a sectional view showing another embodiment of the contact

combustion-type gas sensor before the poisoning process employed in the present invention.

FIG. 7 (A) to (C) are views respectively showing pores of the metal oxide sintered body that constitutes the contact combustion-type gas sensor, the state of the oxidation catalyst adhered to the metal oxide sintered body, and the poisoned state.

FIG. 8 (A) and (B) are views respectively showing the state of the oxidation catalyst penetrating the pores of the metal oxide sintered body that constitutes the contact combustion-type gas sensor, and the poisoned state.

FIG. 9 is a view showing an embodiment of the device for performing poisoning of the contact combustion-type gas sensor.

FIG. 10 is graph showing the relation between the boiling point and the gasifiable concentration by temperature.

FIG. 11 (A) and (B) are graphs respectively showing the changes in the sensitivity over time in an environment of actually using the contact combustion-type gas sensor and when silicon compounds are forcefully adhered.

BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the present invention will now be explained with reference to the drawings.

FIG. 1 (A) and (B) respectively show one embodiment of a gas detecting element 1 that constitutes the contact combustion-type gas sensor of the present invention. A heater 2, which is a resistance wire having heat resistance and corrosion resistance formed into a coil shape, is stretched between stays 3 and 4 which also function as leads. Around the heater 2 is formed an induction portion 5 by mixing an oxidation catalyst powder and an insulating powder of a predetermined composition with a liquid such as

water to make a slurry, dripping the slurry onto the heater 2 to form a spherical shape, solidifying it by natural drying, and then sintering it.

Reference number 6 in the drawing denotes a base that fixes the stays 3 and 4 and attaches to a case described later.

5   One or a plurality of types of oxidation catalyst powder is chosen from platinum (Pt), palladium (Pd), platinum oxide (PtO) and palladium oxide (PdO) that is processed into fine powder by passing through a grinding step or the like. The oxidation catalyst powder is mixed with heat-resistant insulating powder such as alumina and silicon oxide to not less than 30 percent by weight and preferably not less than 40 percent by weight.

10   The gas detecting element 1 constituted thus is housed in an atmosphere including in the form of a vapor at not less than 10 ppm a material that exerts a poisoning action on the oxidation catalyst, such as silicon, at a concentration higher than the actual measuring environment. Aging of the induction portion 5 is performed for a specified time, such as 2 hours, by heating to a range between 180°C and 500°C by means of Joule

15   heat generated from the heater 2 by energizing the stays 3 and 4.

Since the speed in which the aging advances greatly depends on the temperature of the induction portion 5, setting the temperature of the induction portion 5 higher can shorten the aging time.

Thus, the silicon vapor present in the environment reacts with the oxidation

20   catalyst of the induction portion 5 to become silicon dioxide that adheres to the surface of the induction portion 5. At the stage when the specified time has elapsed, energizing of the stays 3 and 4 is stopped, and the induction portion 5 is removed from the aging environment.

To investigate the concentration of the oxidation catalyst powder in the

25   induction portion 5 of the gas detecting element 1 and the sensitivity to flammable gas

from said aging process, as shown in Table 1, samples were prepared in which the

oxidation catalyst powder content of the induction portion 5 was altered.   These samples

were then aged for 20 hours in an atmosphere in which hexamethyldisiloxane is present

as a silicon vapor at 2,000 ppm.

5   [Table 1]

Symbol	Insulating Powder AI_2O_3 (wt%)	Oxidation Catalyst Powder		Total Catalyst Quantity (wt%)
		Pd (wt%)	Pt (wt%)	
●	92	7	1	8
■	82	13	5	18
○	67	22	11	33
□	45	45	10	55
△	0	80	20	100

FIG. 2 shows changes in sensitivity in an environment containing silicon vapor

after adjusting the initial indicated value of the gas detecting element manufactured in the

aforementioned process to a specified value.   In the graph, Group A shows the

10   characteristics of the gas detecting element in which the concentration of the oxidation

catalyst powder in the induction portion 5 is not less than 30 percent by weight and

preferably not less than 40 percent by weight, and group B shows the characteristics of

the gas detecting element in which the oxidation catalyst powder in the induction portion

5 is not more than 30 percent by weight.   As is clear from FIG. 2, for the gas detecting

15   element in which the concentration of the oxidation catalyst powder in the induction

portion 5 is not less than 30 percent by weight and preferably not less than 40 percent by

weight, the decrease in sensitivity was extremely small, as is also evident from the curve

of group A. In contrast, for the gas detecting element in which the oxidation catalyst powder in the induction portion 5 is not more than 30 percent by weight, not only did the sensitivity fall rapidly at the early stages as shown in the group B of FIG. 2, but the sensitivity fell over time as well.

5   Meanwhile, FIG. 3 shows the results of investigating fluctuations in sensitivity in an environment containing silicon vapor after adjusting the initial indicated value of the gas detecting element manufactured in the aforementioned process to a specified value without performing the aforementioned aging process on the gas detecting element shown in the aforementioned Table 1.

10   That is, group A in FIG. 3 shows the characteristics of the gas detecting element in which the concentration of the oxidation catalyst powder in the induction portion 5 is not less than 30 percent by weight and preferably not less than 40 percent by weight, and group B shows the characteristics of the gas detecting element in which the oxidation catalyst powder in the induction portion 5 is not more than 30 percent by weight. As is

15   evident from FIG. 3, a gas detecting element that contains an oxidation catalyst powder concentration of not less than 30 percent by weight and preferably not less than 40 percent by weight has an extremely small drop in sensitivity, as also seen from the curve of group A. In contrast, for the gas detecting element in which the oxidation catalyst powder in the induction portion 5 is not more than 30 percent by weight, not only did the

20   sensitivity fall rapidly at the early stages as shown in group B of FIG. 3, but the sensitivity fell over time as well.

From this it is found that setting the concentration of the oxidation catalyst powder to not less than 30 percent by weight and preferably not less than 40 percent by weight can prevent a decease in the initial sensitivity due to silicon vapor and maintain

25   the sensitivity at a stable, high level over a long period of time regardless of whether

aging is performed in the presence of silicon vapor.

FIG. 4 shows an embodiment of the gas detecting element, wherein on the surface of the induction portion 5 described in the aforementioned embodiment there is further formed a catalyst layer 7 by applying a slurry consisting only of an oxidation

5   catalyst powder, and sintering it.

The gas detecting element constituted thus is placed in the same environment as described above, and then aging is performed by heating the induction portion 5 to between 180°C and 500°C with Joule heat generated from the heater 2 by energizing the stays 3 and 4.

10   According to this embodiment, since the oxidation catalyst powder has a smaller grain size than the heat-resistant insulating substance and silicon adheres to the oxidation catalyst powder, the surface region functions to filter silicon with a relatively large molecular weight, thereby preventing silicon in the measurement environment from invading the induction portion 5, and so more reliably restricting reductions in sensitivity.

15   In the aforementioned embodiment, aging was performed on the gas detecting element 1, but the same effect is exhibited even if aging is performed in the state of being housed in a case and assembled into the contact combustion-type gas sensor.

In the aforementioned embodiment, the induction portion 5 was constituted by dripping a mixed slurry of the oxidation catalyst powder and the insulating powder onto

20   the heater 2, forming a solidified body, and then sintering it.   However, the same effect is exhibited even if sintering is done after forming a solid in a two-step process by dripping only a slurry of the insulating powder onto the heater 2 to form a solid, sintering it, and then dripping a slurry of the oxidation catalyst powder thereon.

Since doing so can selectively impregnate the oxidation catalyst powder at a

25   high concentration near the surface where the gas to be detected makes contact, a cost

savings is achieved and sensitivity fluctuations due to silicon vapor can be minimized as much as possible by raising the concentration of the oxidation catalyst at the induction region.

Incidentally, the built-in heater-type gas sensor described above is particularly

5 effective in detecting flammable gas, such as hydrogen, in the exhaust pipe of the fuel cell system shown in FIG 5.

A fuel cell 10 is constituted by laminating a plurality of groups of fuel cells not illustrated, each consisting of an electrolyte electrode structure in which an electrolyte such as a solid polymer electrolyte membrane is sandwiched between an anode electrode

10 and a cathode electrode and further sandwiched between a pair of separators. Fuel gas such as hydrogen supplied from an inlet side path 11 on the anode side electrode is ionized by a catalytic electrode and moved to the cathode side electrode via the solid polymer electrolyte membrane that is moderately humidified. Electrons that are given off during this period are diverted to an external circuit to be utilized as direct current

15 electrical energy. Since oxidizer gas such as oxygen or air is supplied to the cathode side electrode via an inlet side path 12, water is produced at the cathode side electrode by the reaction of the hydrogen ions, electrons and oxygen. Then, at the cathode side, so-called off gas is discharged to outside the system from outlet side paths 13, 14 on the anode side and cathode side, respectively.

20 Here, a contact combustion-type gas sensor 15 of the present invention, to which a poisoning procedure has been applied, is installed at the outlet side path 14 of the cathode side, and confirmation that hydrogen gas has not been discharged from the outlet side path 14 of the cathode side is performed by a monitoring device 16.

According to this embodiment, even if organic silicon packing and hoses are

25 used for the outlet side path 14 on the cathode side that reaches a high temperature

compared to other gas paths, hydrogen gas can be detected without causing changes in sensitivity over time.

A second embodiment of the contact combustion-type gas sensor of the present invention will now be described in detail.

5   The contact combustion-type gas sensor of the present invention supports a catalyst on a carrier made of a metal oxide sintered body adhered to a resistance thermometer bulb.   As a metal oxide used for this element, at least one kind chosen from alumina, silica, or zeolite is given.

In the present invention, zeolite is preferable from the aspect of easily
10   controlling the pore diameter of the metal oxide sintered body.   Also, as the oxidation catalyst used for the contact combustion-type gas sensor, one is suitably selected from the group of platinum, ruthenium, palladium, and rhodium depending on the type of flammable gas to be detected.

FIG. 6 shows an example of the contact combustion-type gas sensor as a basic
15   element.   A contact combustion-type gas sensor 21 consists of, for example, a platinum wire with a diameter of 60 μm wound 10 times with an outer diameter of 0.6 mm to produce a resistance thermometer bulb 22 that also functions as a coil heater with a length of 1.5 mm.   Next, an alumina, silica, or zeolite paste is stuck to the resistance thermometer bulb 22, which is then fired at 800°C to form a porous metal oxide sintered
20   body 23 having electrical insulation on the platinum coil.

Here, the pore diameter of the metal oxide sintered body 23 is preferably smaller than the organic silicon and greater than a flammable gas molecule, an oxygen molecule, and a water molecule.

The metal oxide sintered body 23 is then immersed in a platinum chloride acid
25   solution, and the platinum chloride acid solution is made to impregnate pores 24 (FIG. 7

(A)) of the metal oxide sintered compact 23 (FIG 7 (B)).   When the impregnation is

sufficiently completed, the metal oxide sintered body 23 is raised, heating decomposition

is carried out at 600°C so that catalyst particles 25 of a platinum catalyst are carried on

the pores 24 and the surface of the metal oxide sintered body 23.

5   Since the contact combustion type gas sensor 21 constituted in this way has

pores 24 that are smaller than the organic silicon and greater than a flammable gas

molecule, an oxygen molecule, and a water molecule, flammable gas molecules and

oxygen molecules can reach the catalyst particles 25 being carried in the pores 24 of the

metal oxide sintered body 23.

10   On the other hand, organic silicon adheres to the surface of the catalyst particles

25 that are fixed to the surface of the metal oxide sintered body 23 (FIG 7 (C)).

The aforementioned embodiment described the case of catalyst particles 25

impregnating the pores of each particle of the metal oxide sintered body 23.   However,

as shown in FIG 8 (A), since the organic silicon can permeate only into the region near

15   the surface (the top side in the drawing) in the mode of the catalyst particles 25

permeated into gaps formed between particles of the metal oxide sintered body, only the

catalyst particles 25 on the surface are covered by organic silicon.

The base of the contact combustion-type gas sensor 21 constituted in this way is

accommodated in a process chamber 30 as shown in FIG 9.   Organic silicon such as

20   hexamethyldisiloxane or hexamethyldisilazane, which is the poisoning component, is

supplied to this space from a vaporizer at a concentration of 10 to 1,000 ppm.   Electric

power is simultaneously supplied from a power unit 32 to the resistance thermometer

bulb 22 of the contact combustion-type gas sensor 21 to heat to between 130°C and

500°C the contact combustion-type gas sensors 21 to be processed.

25   In addition, the organic silicon must be easy to obtain industrially, and have a

vapor pressure sufficient for reaching a concentration necessary for the processing.

Table 2 shows examples of the organic silicon.

[Table 2]

Organic Silicon Compound	Boiling Point (℃)	Gasifiable concentration (%) at normal temperature
Tetraethoxysilane	166	0. 2
Octamethylcyclotetrasiloxane	175	0. 1
Tetramethylsilane	26. 5	73. 7
Trimethylsilane	6. 7	100
Tetramethylcyclotetrasiloxane	135	0. 9
Hexamethyldisilane	113	3. 0 (estimate)
Hexamethyldisilazane	125	1. 6 (estimate)
Hexamethyldisiloxane	101	5. 3
Dimethyldimethylaminosilane	67	19. 7
Dimethyldimethoxysilane	81. 4	11. 8

5   As shown in FIG. 10, there is a correlation between the boiling point of organic

silicon and the concentration at which it is gasifiable at an normal temperature, in that as

the boiling point rises it does not gasify until reaching a specified concentration.   The

organic silicon easily gasifies as the boiling point decreases, but does not gasify even at a

normal temperatures, and so handling is not easy.   Hexamethyldisiloxane,

10   hexamethyldisilazane, and hexamethyldisilane, which are in a range of 50°C to 150°C,

are readily obtainable and can be easily adjusted to the concentration required for

processing.

Moreover, in the case of the concentration of the organic silicon being 10 ppm or

less, not only does the time to the completion of processing, that is, the time until the

15   sensitivity drop reaches the converging point, become longer, but since the quantity of

organic silicon decreases, measurement errors easily arise, leading to a drop in the

processing yield.

Meanwhile, when the organic silicon concentration exceeds 30,000 ppm, the

evaporation rate of the organic silicon is significantly influenced by the temperature, which leads to a drop in the processing yield.

Accordingly, the lower limit of the organic silicon concentration is 10 ppm and the upper limit is 30,000.   However, in consideration of accuracy and ease of adjusting
5   the atmosphere, and moreover the manufacturing yield, the organic silicon concentration is preferably between 100 ppm and 20,000 ppm.

Since the catalytic action of an oxidation catalyst is low when the temperature is 130°C or less, the decomposition rate of organic silicon is also low, so that adhesion of a silicon compound 26 to the surface of the metal oxide sintered body 23 does not advance.
10   On the other hand, if the temperature is 500°C or more, sintering of the metal oxide sintered body 23 will arise, causing the catalytic action of the oxidation catalyst to fall.

The organic silicon is thus decomposed on the surface of the metal oxide sintered body 3 heated to several hundred degrees, and as shown in FIG 7 (C) and FIG 8 (B) becomes a silicon compound 26 that adheres in a laminar form.   When removed
15   from the process chamber 10 after the predetermined time, the contact combustion-type gas sensor 1' of the present invention is complete.   When the above-mentioned silicon compound 26 is analyzed by X-ray electron spectroscopy, it is confirmed as being silicon dioxide.

In addition, although the processing time is influenced by the concentration and
20   temperature of the organic silicon, since it is a value uniquely determined by these parameters, the processing time can be determined by prior experimentation.

Although that portion of the oxidation catalyst which is exposed to the surface of the contact combustion-type gas sensor 21' constituted in this way is covered by the silicon compound 26, thereby losing its catalytic function, entry of organic silicon is
25   impeded by the silicon compound 26 formed on the surface of the sensor 21'.   Moreover,

since the pores 24 of the metal oxide sintered body 23 are smaller than the silicon

compound 26 and larger than a flammable gas molecule, an oxygen molecule, and a

water molecule, the catalyst particles 25 positioned inside the pores 24 are presumed to

be able to maintain their function as an oxidation catalyst.

5   For the purpose of comparison, the contact combustion-type gas sensor 1 before

processing and the contact combustion-type gas sensor 21' after processing were

disposed in an environment in which organic silicon is present to investigate changes in

the sensitivity to detecting flammable gas over time.   As shown by line A in FIG. 11 (A),

there was hardly any change over time in the detection sensitivity of the contact

10   combustion-type gas sensor 21' of the present invention.

On the other hand, the oxidation catalyst layer does not have a pore diameter

that is smaller than the organic silicon and larger than a flammable gas molecule, an

oxygen molecule, and a water molecule.   Also, in the contact combustion-type gas

sensor 21 to which the aforementioned processing is not applied, the tendency of the

15   sensitivity to slowly decrease over time continues without converging at a steady value,

that is, without settling at a steady value.

In the aforementioned embodiment, processing is performed in the environment

in which organic silicon is present, but when processing is executed in an environment in

which hydrogen is added, the detection sensitivity decreases in a short time to a specified

20   sensitivity as shown by line A in FIG. 11 (B).   This is presumed to happen because,

when processing is executed in an environment in which organic silicon and hydrogen

are present, hydrogen contained in the atmosphere will combust on the surface due to the

oxidation catalyst of the contact combustion-type gas sensor 1, and so the surface

temperature of the contact combustion-type gas sensor 1 becomes higher than the case

25   when heated only by a resistance thermometer bulb (that is, a state without an oxidation

catalyst), thereby promoting the adhesion of organic silicon.

Line B in FIG. 11 (B) shows the drop in sensitivity due to processing in an atmosphere in which hydrogen is not added.

If the amount of hydrogen added has a concentration of 100 ppm to 40,000 ppm

5   with respect to 10 to 30,000 ppm for organic silicon vapor, such as hexamethyldisiloxane or hexamethyldisilazane, the silicon compound 6 can be generated safely and in a short time even if hydrogen, a flammable gas, is used.

When the hydrogen concentration is 100 ppm or less, similarly to when the organic silicon concentration is extremely low, the time until the completion of

10   processing, that is, the time until the sensitivity drop settles at a fixed value, or, reaches the converging point, becomes longer.   Also, it is not desirable for the hydrogen concentration to exceed 40,000 ppm on grounds of work safety, since the lean flammability limit is exceeded.

In consideration of these matters, the hydrogen concentration is between 100

15   ppm and 40,000 ppm, and in consideration of safety and processing efficiency, more preferably between 1,000 ppm and 20,000 ppm.

In addition, although the time to the completion of processing is influenced by the concentration and temperature of the organic silicon and hydrogen, since it is a value uniquely determined by these parameters, the processing time can be determined by prior

20   experimentation.

If the above-mentioned contact combustion-type gas sensor 21' is placed in an environment in which organic silicon is mixed to detect flammable gas, such as hydrogen, then oxygen and the flammable gas will pass through the pores 24 of the metal oxide to reach the catalyst 25 and ignite, producing the predetermined output.   Meanwhile, since

25   the substance which serves as organic silicon is impeded by the silicon compound 26

formed in advance on the surface of the sensor 1', and, moreover, the diameter of the pores 24 of the metal oxide sintered body 23 is smaller than the organic silicon, it is presumed not to be able to enter as far as the catalyst particles 25 positioned inside the pores 24, and so does not cause a drop in sensitivity.

5   As mentioned above, compared with the contact combustion-type gas sensor with no poisoning treatment, the decrease in sensitivity of the sensor of the present invention is extremely small, and so the detection sensitivity at the start of usage can be stably maintained over a long period.

The aforementioned embodiment was constituted by forming the metal oxide sintered body to enclose a coiled resistance wire, but it is clear that the same action is exhibited even if applied to a sensor in which the metal oxide sintered body is formed in a laminar form on the surface of a plate-shaped heater.

Incidentally, the aforementioned sensor with the built-in heater is particularly effective for detecting flammable gas, such as hydrogen, in the exhaust pipe of the fuel cell system shown in FIG. 5.

According to this embodiment, similarly to the aforementioned embodiment, even if organic silicon packing and hoses are used for the outlet side path 14 on the cathode side that reaches a high temperature compared to the other gas path, hydrogen gas can be detected without causing changes in sensitivity over time.

20   Since it has few drops and fluctuations in sensitivity due to silicon in the atmosphere, the contact combustion-type gas sensor of the present invention can detect flammable gas such as hydrogen without causing fluctuations in sensitivity over time even when in an environment in which silicon vapor emitted from packing and tubes is present due to high temperature such as found in the gas outlet path on the cathode side

25   of a polymer-type fuel cell.